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[2+2] Cycloaddition Reaction as a Tool to Monitor the Formation of Thermodynamically Stable Ladder Coordination Polymers

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Supporting Information

Experimental Section:

Materials and General Methods. All chemicals purchased were of reagent grade and were used without further purification. The elemental analyses were carried out at the Elemental Analysis Laboratory, CMMAC, Department of Chemistry, National University of Singapore. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of $5^{o}C\ min^{-1}$ using a SDT 2960 Thermal Analyser. The NMR spectra were recorded with a 300 MHz FT-NMR spectrometer with TMS as internal reference. For all the NMR spectra recorded, a drop of HNO_3 was added to dissolve the insoluble samples **1** – **3**, as well as to dissociate the paramagnetic metal ions from the organic ligands. Powder X-ray diffraction patterns (PXRD) were recorded on a Siemens D500 diffractometer with graphite monochromatized Cu-Kα radiation (λ = 1.54056 Å) at room temperature (23°C). Variable temperature X-ray powder diffraction was recorded using a Bruker – AXS D8 advance powder X-ray diffractometer with an Anton Paar Model HTK 1200 high temperature chamber.

Synthesis of [Cu(O_2CCF_3)$_2$(μ-bpe)(DMF)] (1). Trifluoroacetic acid (3.2 ml, 0.4 mmol) and bpe (36.4 mg, 0.2 mmol) in DMF (2 ml) were added consecutively to a solution $Cu(CH_3COO)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) in DMF solution (2 ml). Slow evaporation of the clear aqua-blue solution resulted in blue hexagonal platy crystals of **1** (34.5g, 27.57%) in a day. ^{1}H-NMR δ_H (300 MHz, D_2O), 8.70 (4H, d, pyridyl protons), 8.18 (4H, d, pyridyl protons), 7.80 (2H, s, -CH=CH-), 2.91 (3H, s, DMF protons), 2.76 (3H, s, DMF protons). Elemental analysis (%) Found: C, 42.36; H, 2.85; N, 7.86 Calcd for $Cu(TFA)_2(bpe)(DMF)$ = $CuC_{19}H_{17}F_6N_3O_5$: C, 41.88; H, 3.14; N, 7.71. Thermogravimetric analysis shows the DMF weight loss: Calcd 13.4%, found 14.0%.

Synthesis of [Cu (O_2CCF_3)$_2$(μ-bpe)] (2). Compound **1** was heated at 140°C in N_2 flow for 8 h to obtain pale blue crystals., ^{1}H-NMR δ_H (300 MHz, D_2O), 8.70 (4H, d, pyridyl protons), 8.18 (4H, d, pyridyl protons), 7.80 (2H, s, -CH=CH-). Elemental analysis (%) Found: C,

40.34; H, 2.31; N, 5.61. Calcd for Cu $(TFA)_2$(bpe) = $CuC_{16}H_{10}F_6N_2O_4$: C, 40.73; H, 2.14; N, 5.94. Thermogravimetric analysis shows no weight loss until 240°C.

UV irradiation. The UV irradiation experiments were conducted by using Max 150 xenon light source (150W) of 100% intensity and a radiation of wavelength 350 nm.

Conversion of 2 to [Cu $(O_2CCF_3)_2$ (μ- *rctt* - tpcb)] (3). Compound **2** was irradiated under UV lamp for 48 h to obtain pale blue crystals of **3.** ^{1}H-NMR δ_H (300 MHz, D_2O), 8.59 (8H, d, pyridyl protons), 7.91 (8H, d, pyridyl protons), 5.34 (4H, s, cyclobutane protons). Elemental analysis (%) Found: C, 40.34; H, 2.51; N, 5.76 Calcd for Cu $(TFA)_2$(μ- *rctt* - tpcb) = $CuC_{16}H_{10}F_6N_2O_4$: C, 40.73; H, 2.14; N, 5.94. Thermogravimetric analysis shows no weight loss till 230°C.

X-ray Crystallography. Intensity data for **1** was collected at 223(2) K on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα (λ = 0.71073 Å) radiation using a sealed tube (2.4 kW). An empirical absorption correction was applied to the data using the SADABS[24] program. Both the structures were solved by using direct methods and refined on F^2 by full- matrix least squares procedures with SHELXTL[25, 26].

Crystal data as well as details of data collection and refinement are summarized in Table 1.

Compound	**1**
Empirical Formula	$C_{19}H_{17}CuF_6N_3O_5$
Formula Weight	544.90
Temperature	100(2) K
Wavelength λ, (Å)	0.71073
Crystal System	Monoclinic
Space Group	$P2_1/n$
a(Å)	13.932(11)
b(Å)	9.926(8)
c(Å)	17.741(13)
β, (deg)	112.950(2)
V, (Å^3)	2259.3(3)
Z	4
D_{calcd}, Mg cm^{-3}	1.602
Absorption Coefficient μ,mm^{-1}	1.052
F(000)	1100
Crystal Size, mm^3	0.46 x 0.26 x 0.10
Theta range for data collection(°)	2.37 to 25.00
Index Ranges	-16<=h<=16, -10<=k<=11, -21<=l<=19
Reflections Collected	12731
Independent reflections	3984 [R(int) = 0.0587]
Completeness to theta = 25.00°	99.9%
Data[I> 2σ(I)]/ restraints/ params	3984 / 301 / 395
GOF on F^2	1.045
Final R indies[I> 2σ(I)][a,b]	R1 = 0.0640, wR2 = 0.1519

Final R indies (all data) [a,b]	R1 = 0.0773, wR2 = 0.1615
Largest diff. peak and hole	1.155 and -0.777 e.Å^{-3}

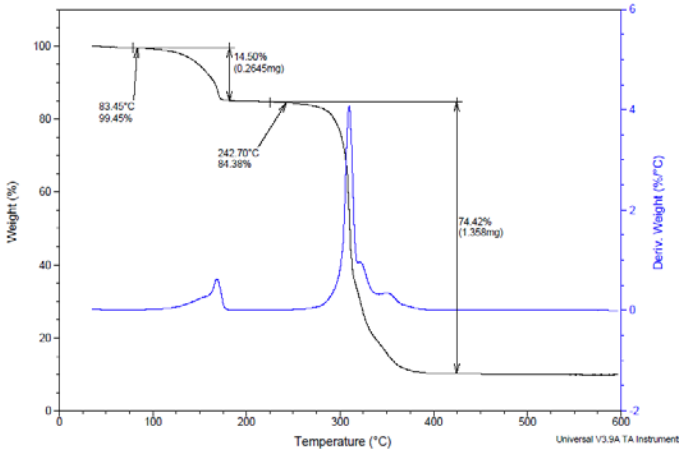

Figure S1: TGA curve of **1**, showing the DMF weight loss of 14.0% in the range 80 to 170ºC.

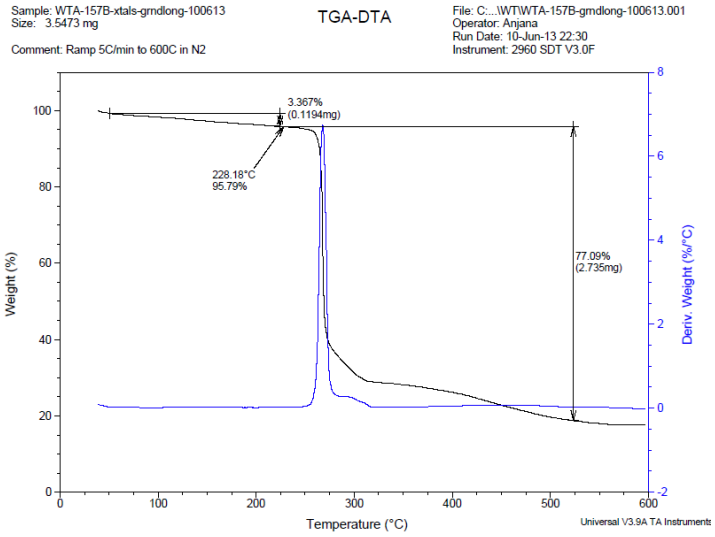

Figure S2: TGA curve of **1** after grinding for 30 min, showing the DMF weight loss of 3.4% in the range 50 to 170ºC.

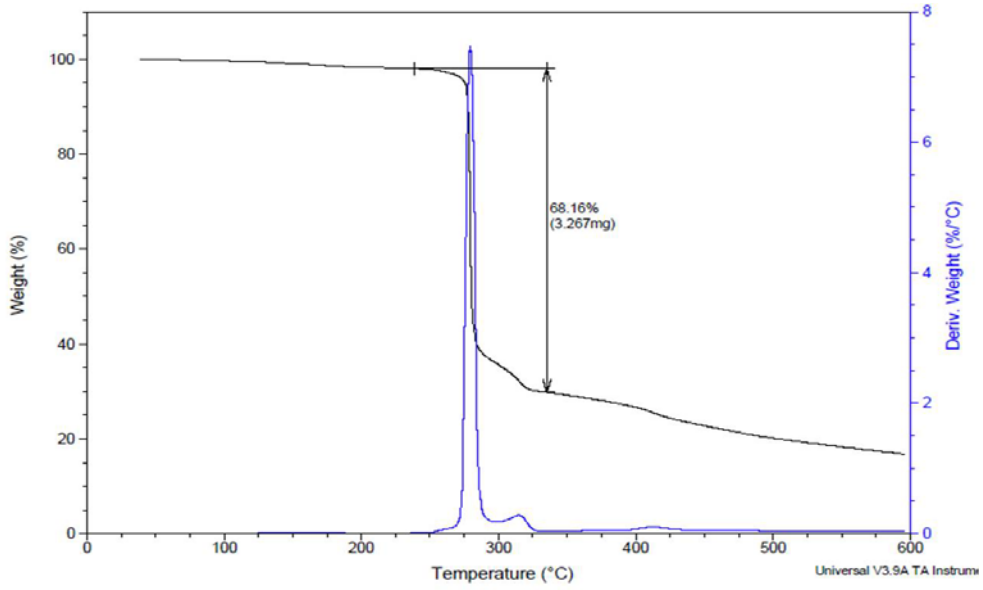

Figure S3: TGA curve of **2**.

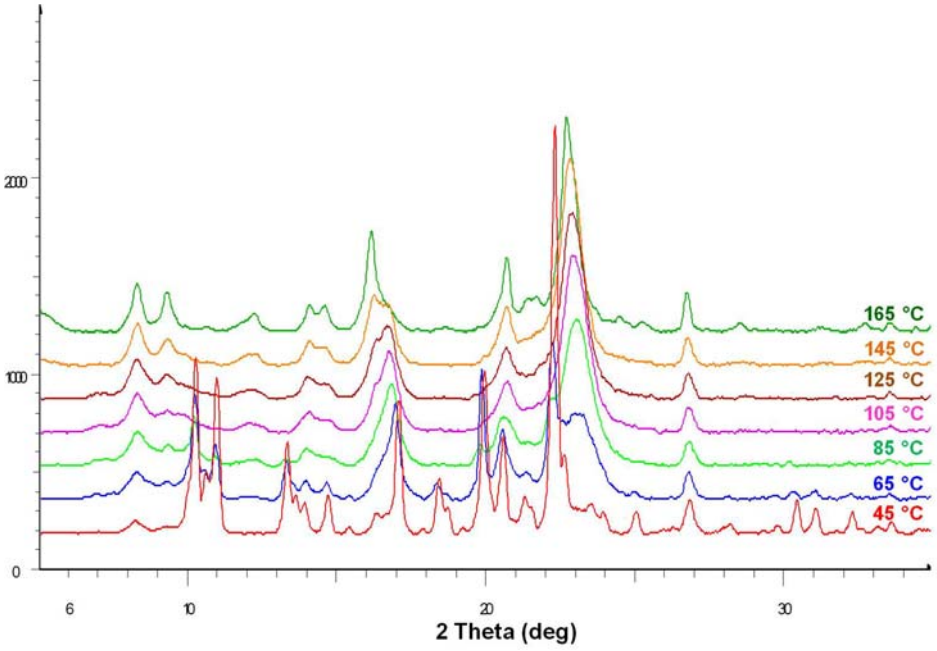

Figure S4: Variable temperature PXRD of cpd **1** from RT to 165 °C in vacuum shows the gradual change of phase from 65°C to a complete new phase at 165°C.

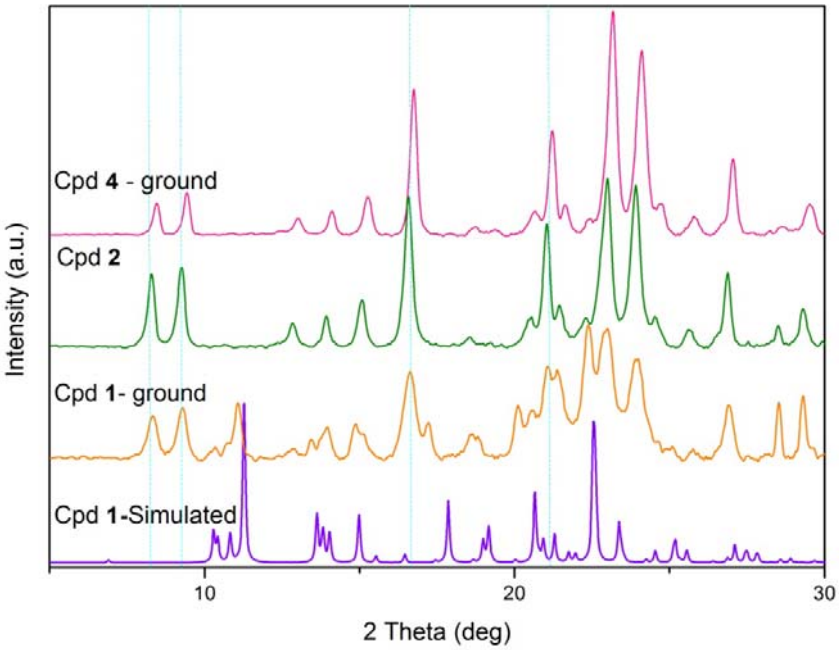

Figure S5: PXRD pattern of cpd **1**, cpd **1** after grinding, cpd **2** and cpd **4** after grinding.

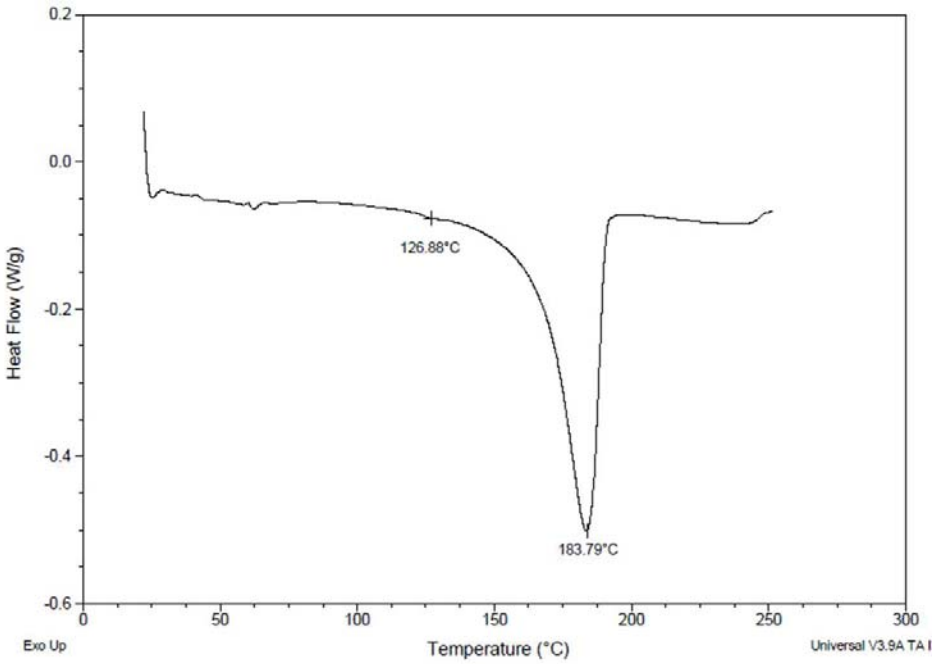

Figure S6: DSC curve of **1**,

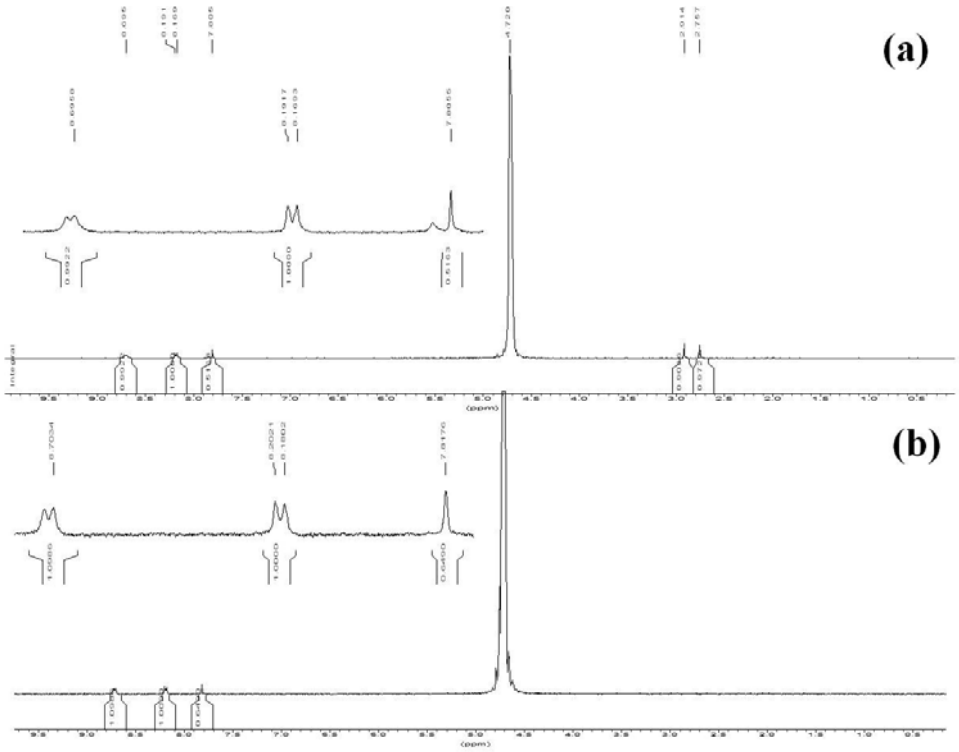

Figure S7: ^{1}H-NMR analysis of (a) Compound **1** and (b) Compound **2**

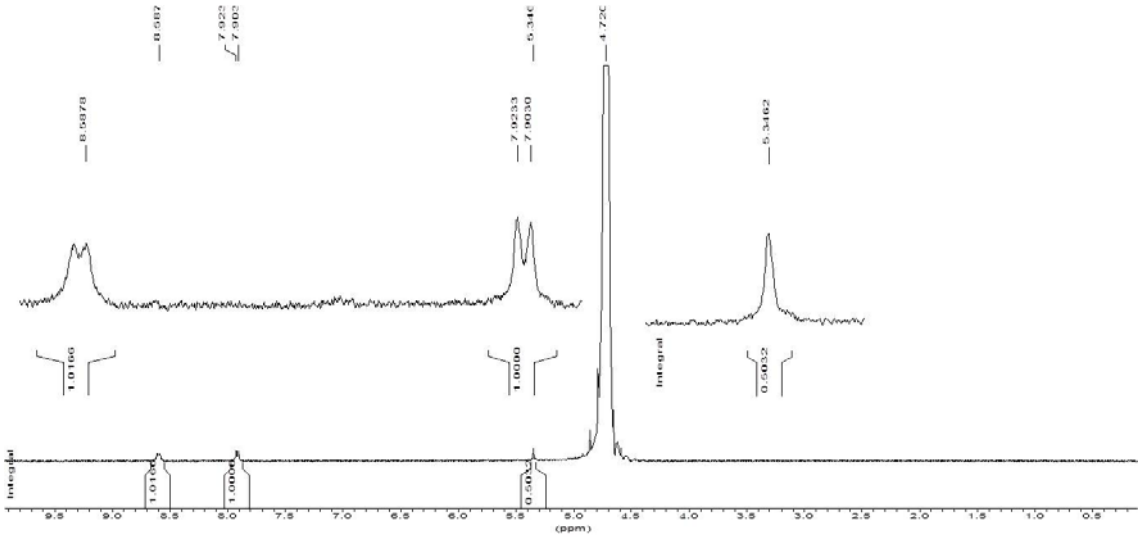

Figure S8: ^{1}H-NMR analysis of Compound **3**